Imaging individual dopant atoms on cleavage surfaces of wurtzite-structure compound semiconductors

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We report the identification of bulk-dopant atoms in $(11\bar{2}0)$ and $(10\bar{1}0)$ cleavage surfaces of wurtzite CdSe in atomically resolved scanning tunneling microscopy images. The In dopant atoms give rise to elevations (hillocks) of up to 5 nm in diameter in the empty- and occupied-state images. This contrast is simulated and it shows that the dopant atoms are positively charged. Hillocks with different symmetries with respect to the underlying lattice are correlated with different subsurface locations of the In-dopant atoms. Dopant atoms can be observed up to a depth below the surface of 3 to 5 layers. A quantitative analysis of the concentration of dopant atoms in the bulk yield the same values for both surfaces and agrees well with the In content of the crystal. Similar features in CdS$(10\bar{1}0)$ surfaces are also attributed to In-dopant atoms.
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I. INTRODUCTION

Doping with foreign atoms provides the basis for most applications of semiconductors. The achievement of the desired dopant profiles depends, however, not only on the development of suitable growth techniques and dopant incorporation procedures. Similarly important are accurate characterization techniques, which provide an atomic-scale insight in the grown structures and lead to a quality feedback. The scanning tunneling microscope can image individual dopant atoms with atomic resolution,[1–17] and thus is ideally suited for this task. However, so far dopant atoms could only be imaged on cleavage surfaces of cubic III-V compound semiconductors. Recently, compound semiconductors grown in the wurtzite structure attracted considerable attention, because of their promising properties for blue-laser applications, although still many doping difficulties persist. Therefore, we investigated the possibility to image individual dopant atoms on cleavage surfaces of wurtzite-structure compound semiconductors by scanning tunneling microscopy (STM). We chose CdSe and CdS as a model system and demonstrate that dopant atoms can be observed on both nonpolar $(11\bar{2}0)$ and $(10\bar{1}0)$ cleavage surfaces and in different subsurface layers. A detailed analysis of the contrast, the properties, and the determination of the concentration will be presented. We show that quantitative measurements of the dopant concentrations are possible on both cleavage surfaces.

II. EXPERIMENT

Samples from *n*-type CdSe and CdS single crystals both doped with In (carrier concentrations of 7×10^{18} and $1\times10^{19}\,\mathrm{cm}^{-3}$) were cleaved in *ultrahigh vacuum* (5×10^{-9} Pa) along $(11\bar{2}0)$ and $(10\bar{1}0)$ planes. After cleavage, the samples were immediately investigated by scanning tunneling microscopy without breaking the vacuum. The samples had ohmic contacts, which were obtained by sputtering gold on two faces of the samples followed by an electrical discharge of a capacitor over these contacts. We used electrochemically etched tungsten tips.

The CdSe wafer had an In dopant concentration of $2\times10^{19}\,\mathrm{cm}^{-3}$ according to the manufacturer. A detailed chemical analysis of two samples using the inductively coupled plasma optical-emission spectroscopy (ICPOES) and the inductively coupled plasma-mass spectroscopy (ICPMS) yielded an In concentration of $(0.8\pm0.1)\times10^{19}$ and $(1.4\pm0.1)\times10^{19}\,\mathrm{cm}^{-3}$, respectively.[18] In addition, the crystals contained the isoelectronic dopant Ca in about the same concentration as that of In dopant atoms [between $(0.4\pm0.15)\times10^{19}$ and $(1.5\pm0.5)\times10^{19}\,\mathrm{cm}^{-3}$]. All other impurities occurred in concentrations of at least one order of magnitude smaller than the In concentration. The CdS wafer had, according to the manufacturer, an In concentration of about $5\times10^{19}\,\mathrm{cm}^{-3}$. A chemical analysis revealed, however, large variations of the In content, such that a quantitative analysis of dopant concentrations by STM is not meaningful for the CdS crystal. The isoelectronic dopant Ca occurred in the CdS crystal in about the same concentration as the In dopants too.

III. RESULTS

After cleavage the surfaces consist of flat terraces separated by steps (Fig. 1). On the flat terraces we observe a high concentration of hillocks or elevations in the constant-current images (see magnification of one hillock in the inset of Fig. 1). These hillocks have an extension of up to 5 nm in diameter. They are shown as white contrast areas in the gray scale STM images. The defects give rise to white contrast features not only in the filled but also in the empty density of state images. In Fig. 2 simultaneously measured STM images of filled and empty density of states of the CdSe $(10\bar{1}0)$ surface are shown. Two hillocks are visible in each STM image (marked by $D1$ and $D2$). The magnitude of the elevation is found to depend strongly on the tip structure and tunneling voltage. However, different heights of the elevations were observed for different hillocks independent of the tip condi-

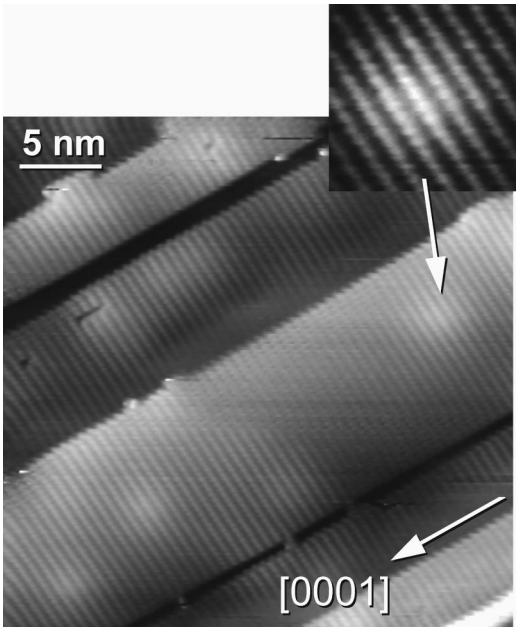

FIG. 1. Constant-current image of the CdSe($10\bar{1}0$) surface obtained at +1.8 V and 0.2 nA. It shows the empty states. Besides steps large elevations can be seen. The inset shows one of these hillocks magnified. They are electrically active In-dopant atoms (see text).

tion. On the CdSe ($11\bar{2}0$) surface hillocks are observed too. They also exhibit a bright contrast in the empty and filled state images and have also essentially the same features and characteristics as those on the CdSe ($10\bar{1}0$) surface.

The extension of the hillocks as well as their voltage dependence indicates the presence of a local band bending.[19] The band bending arises from a localized electrical charge. In this specific case the band bending is imaged as an elevation under positive and negative tunneling voltages. This characteristic is only consistent on *n*-doped surfaces with the presence of a localized positive electrical charge.[4] In the discussion below we will analyze the imaging process in greater detail.

The elevations are superimposed on the atomic-scale corrugation arising from the filled and empty dangling bonds above each Se and Cd atom, respectively.[20–24] No dangling

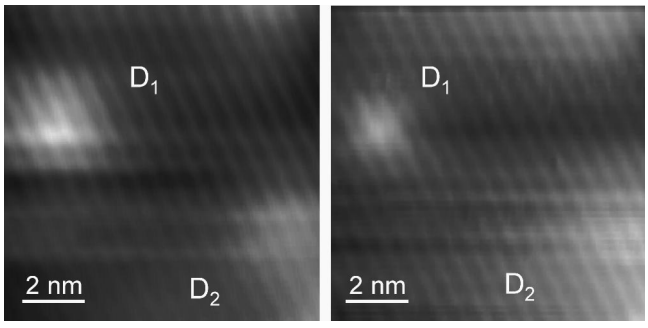

FIG. 2. Simultaneously measured occupied (left, −2.3 V) and empty (right, +2.2 V) density of states images of the CdSe($10\bar{1}0$) surface. Two In-dopant atoms marked by $D1$ and $D2$ can be seen. They give rise to an elevation in both images. The tunnel current was 0.2 nA.

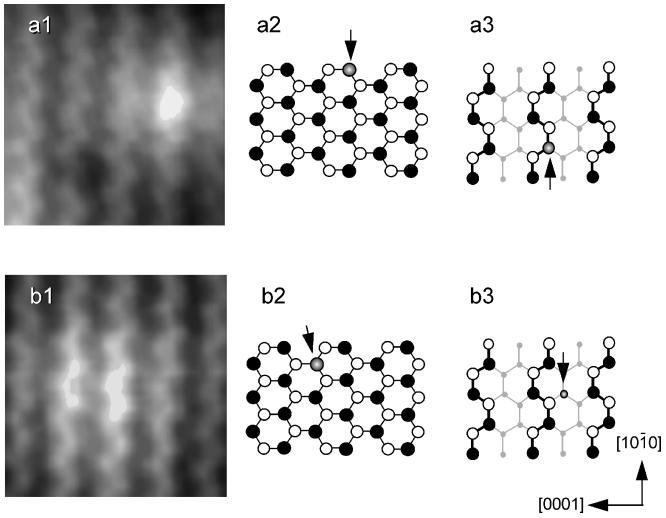

FIG. 3. STM images (frames labeled 1) as well as side (labeled 2) and top views (labeled 3) of a schematic model of In-dopant atoms with different symmetries with respect to the underlying atomic lattice. The STM images were obtained on the CdSe($11\bar{2}0$) surface at +1.9 V and 0.2 nA. The different symmetries are correlated with In-dopant atoms in the first (a) and second (b) subsurface layer.

bond is missing in either the occupied nor the empty-state STM images. Thus, the underlying lattice is not disturbed. However, the relative location of the center of the hillock with respect to the atomic lattice is observed to change between different configurations. In Fig. 3(a) the center of the elevation is located on top of one empty Cd related dangling bond. The feature is very localized. In Fig. 3(b) the center is localized in the center of a unit cell delimited by four Cd atoms. In the occupied states similar changes in symmetry are observed. We focus here on the empty-state images, because the rather complicated crystal structure does not make the determination of the center of the hillocks as easy as on GaAs(110) surfaces. Images of the empty dangling bonds are more favorable for the analysis than images of the occupied states, because an In dopant on a Cd lattice site will give rise to a higher symmetry with respect to the Cd atoms imaged in empty-state STM images. Below we will attribute the different symmetries to dopant atoms incorporated in different subsurface layers. We note that sometimes dopant atoms in deeper layers yield a wider contrast that those in the surface layers, but not a larger magnitude.

The elevations occurred on the ($11\bar{2}0$) and ($10\bar{1}0$) surfaces in concentrations of $(1.2\pm0.3)\times10^{12}$ and $(1.25\pm0.3)\times10^{12}\,\mathrm{cm}^{-2}$, respectively. These concentration values are the sum of all observable hillocks, independent of their symmetry.

We observed similar elevations on the In-doped CdS($10\bar{1}0$) surface (Fig. 4). The extension of the elevations was up to 5 nm in diameter. Also, on CdS surfaces the elevations were the pointlike defects occurring in largest concentrations (with the exception of some vacancies, which appear as one missing dangling bond). The CdS samples investigated for comparison had an In-doping concentration in the same order of magnitude as the CdSe samples. However, due to the inhomogeneity of the In distribution within

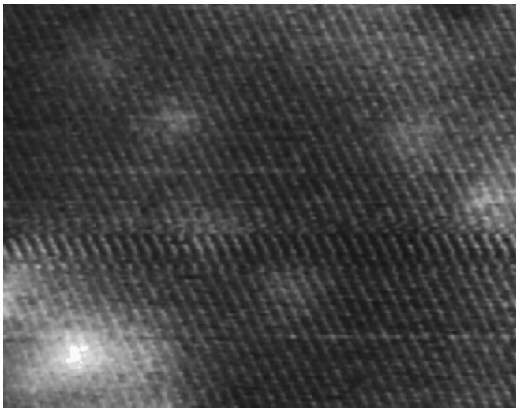

FIG. 4. Constant-current image of the empty states of the CdS$(10\bar{1}0)$ surface. Hillocks similar to those on CdSe surfaces can be observed. The image has been measured at +2.5 V and 0.3 nA.

the crystal we cannot provide a reasonable average value. The measurement on CdS are only intended to demonstrate that the features attributed to In dopant atoms occur on cleavage surfaces of other In-doped II-VI wurtzite-compound semiconductors too.

IV. DISCUSSION

First we address the origin of the hillocks. The observation that no dangling bond is missing, and thus the crystal lattice is not disturbed rules out the presence of any vacancy-related defect. Indeed we observed defects on the CdSe cleavage surfaces, which we attribute to vacancies. Vacancies have an atomically localized missing dangling bond. The missing dangling bonds are not surrounded by a long-range elevation. Thus, vacancies are not charged and cannot be identical with the defects giving rise to the contrasts described above. We attribute, therefore, the hillocks to impurities. Only In and Ca impurities have concentrations in the crystal large enough to account for the hillocks. The element In is an *n*-type dopant in CdSe and CdS. It has three valence electrons and will be localized on a Cd site with two valence electrons. Thus, an electrically active In dopant is positively charged. Ca is an isoelectronic dopant. It should not change the electronic properties and be localized on a Cd site too. In such a configuration it is uncharged. From this we conclude that the elevations are the signature of the electrically active In dopant atoms. The elevations cannot be due to adsorbates, because they can be observed in constant concentration directly after cleavage already.

The dopant atoms appear as elevations in the occupied- and empty-state images. This particular contrast has been observed for Si_{Ga} donors in *n*-doped GaAs(110) surfaces too.[4,16] It can be explained as follows: At positive-sample voltage the downward band bending induced by the positive charge of the dopant increases the number of empty states available for tunneling into the surface. Thus, the dopant atom is surrounded by an elevation. At negative-sample voltages the tip-induced band bending causes the electrons to accumulate in the near-surface region. Electrons thus tunnel out from the valence-band states and from filled states near the conduction-band edge in the accumulation layer. The band bending reduces the number of valence-band states, but increases the number of filled states in the conduction band available for the tunneling process.[4] In addition, the charge of the dopant atom induces a local downward screened Coulomb potential.[25] This affects the number of filled states by increasing the band bending locally. The polarity of the contrast depends on the relative densities of states lost and gained (weighted with the transfer coefficient of the tunneling process) by the combined effect of the tip- and charge-induced band bending.

In a simple approach the contrast induced by a localized electrical charge can be simulated using the following assumptions and procedures. The tunnel current is proportional to the energy-integrated density of states of the surface times the transfer coefficient in the energy window from the Fermi level to the Fermi level plus the applied voltage, times the electron charge. This approach assumes a metallic tip with no strong variation in the density of states. The densities of states of the valence and conduction bands of CdSe are modeled using parabolic bands and the respective masses of the electrons and holes (taken from Ref. 26). It is assumed that the surface is unpinned. This is the case for the CdSe cleavage surface.[20–24] The presence of the dopant induces the additional screened-Coulomb potential. In a WKB-like approximation the Coulomb potential can be added to the energies of the clean CdSe surface. We modeled the screened-Coulomb potential with a Gauss potential fitted to the experimentally measured interaction potential between single positively charged P vacancies on InP(110).[25] The calculation of the current has been performed for a line cut through the center of the dopant atom. The tip-induced band bending has been calculated according to Ref. 27 and is taken into account. Finally, the current is normalized with the current obtained for a calculation without the presence of the dopant (current far away from the dopant atom). The only free parameter in the calculation is the tip-sample separation. It is fixed to 0.5 nm, since at this distance the calculation reproduces all contrast features of charged defects and dopants on cubic III-V compound semiconductors.[28] In addition, a separation of 0.5 nm agrees with generally accepted tip-surface distances. Figure 5 shows the results of the simulation. The tunnel current increases close to the dopant atom for both the empty and the occupied density-of-states images, in agreement with the experimental result. This corroborates the explanation of the contrast of the In-dopant atoms. The increased current induces a retraction of the tip from the surface. This is equivalent to an apparent elevation on the surface as observed. If we assume a negative charge we obtain a different contrast. Thus, the dopant atoms is positively charged close to the surface in agreement with the general expectation.

On GaAs and InP (110) surfaces the different symmetries of the dopant atoms with respect to the underlying lattice have been interpreted as the signature of dopant atoms in different subsurface layers.[2,14] The different symmetries observed for the In dopant atoms on the CdSe cleavage surface can be explained with the same model. Only the different crystal structure makes the comparison somewhat more complicated. We demonstrate this effect for the dopant atoms in the CdSe$(11\bar{2}0)$ surface. Similar effects occur for dopant atoms in the $(10\bar{1}0)$ surface too.

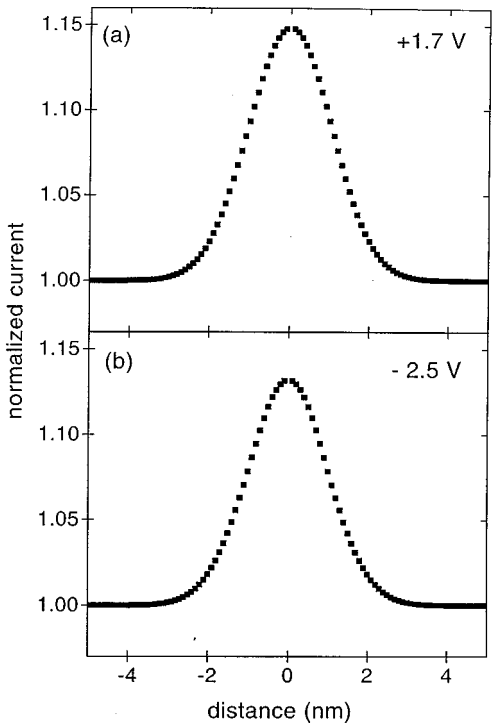

FIG. 5. Simulation of the normalized current of a positive charge on a CdSe surface. A line cut through the center of the charge-induced screened Coulomb potential approximated by a Gaussian function is shown at a tip-surface separation of 0.5 nm.

The structure of the $(11\bar{2}0)$ surface with its zigzag chains make the analysis somewhat complicated, but if we focus on the Cd sublattice (empty state images) clear symmetries can be extracted. Frames (a2) and (a3) of Fig. 3 show a schematic model in side and top view of an In atom on a first-layer Cd lattice site. Obviously, the center of the hillock must be on top of this atom in agreement with Fig. 3(a1), where the center of the elevation is located on top of one empty dangling bond. A dopant atom in the second layer is located in between two atomic zigzag chains [see frames (b2) and (b3) of Fig. 3]. The mirror plane of the feature perpendicular to the zigzag chains is on top of the Cd dangling bonds. This structure agrees with the STM image in Fig. 3(b1), where the center is localized in the middle of an imaginary unit cell delimited by four Cd atoms. An In dopant in the third subsurface layer has again the same symmetry as one in the surface layer. We note that obviously the contrast can be explained on the basis of a spherical screened Coulomb potential.

From the analysis of the symmetry of the contrasts we know that dopant atoms up to at least the third subsurface layer can be recognized in the STM images. However, the contrast of the dopant atoms is weakening quickly with increasing depth, such that no dopant atoms deeper than the fifth subsurface layer can be identified or imaged reliably. These two limits allow us to calculate the upper and lower limits of the dopant concentrations in the bulk from the surface concentrations of the hillocks. With experimentally observed surface concentrations on the $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces of $(1.2\pm0.3)\times10^{12}$ and $(1.25\pm0.3)\times10^{12}\,\mathrm{cm}^{-2}$, respectively, we obtain ranges for the In-dopant concentration of $(1.3-2.1)\times10^{19}\,\mathrm{cm}^{-3}$ and $(1.1-1.8)\times10^{19}\,\mathrm{cm}^{-3}$, respectively. These ranges agree well with the data of the In concentration available from the manufacturer and from ICPOES/ICPMS measurements $[(0.8-2)\times10^{19}\,\mathrm{cm}^{-3}]$. In particular, the very close agreement of the In concentration measured by STM on the $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces underlines that both surfaces are suitable for concentration measurement and that none of the surfaces affects the imaging of bulk-dopant atoms.

Finally, the observation of dopant atoms on CdSe and CdS demonstrates that not only the material CdSe is suitable for imaging bulk-dopant atoms. It rather suggests that the cleavage surfaces of all wurtzite-compound semiconductors will allow a bulk-dopant assessment from STM images. Furthermore, the similarity of the contrast of In donors in II-VI semiconductors with that of Si donors in GaAs(110) suggests that the imaging process of dopant atoms and charged defects is essentially the same on all unpinned cleavage surfaces of III-V and II-VI compound semiconductors in both the wurtzite and cubic phases.

V. CONCLUSIONS

We identified isolated In-dopant atoms in STM images of cleavage surfaces of wurtzite CdSe and CdS. The dopant atoms give rise to an elevation (hillock) of up to 5 nm in diameter. The contrast of the dopants is explained by a combined effect of the screened-Coulomb potential induced by the localized charge of the dopant, the tip-induced band bending, and the transfer coefficient of the tunneling process. The contrast indicates that the dopant atoms are positively charged. Hillocks with different symmetries with respect to the underlying lattice are correlated with different subsurface locations of the In-dopant atoms. The dopant atoms observed on $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces exhibit the same properties. Dopant atoms can be observed up to the third to fifth subsurface layer. A quantitative analysis of the concentration of dopant atoms in the bulk yield the same values for both surfaces and agrees well with the In content of the crystal. We conclude that bulk-dopant atoms can be imaged well and their concentrations measured on cleavage surface of wurtzite compound semiconductors.

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